Atomic layer deposition of Cu$_2$S for future application in photovoltaics

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Alternating exposure to bis(N,N'-di-sec-butylacetamidinato)dicopper(I) and hydrogen sulfide is shown to produce high quality chalcocite (Cu$_2$S) thin films by atomic layer deposition on silicon and fused silica substrates. The layer-by-layer chemical vapor deposition method enables conformal growth of the phase-pure material at 130 °C. X-ray diffraction reveals that polycrystalline *high*-chalcocite films are deposited preferentially oriented in the ⟨00*l*⟩ plane. The optical properties of this naturally *p*-type absorber compare well with previous reports on single crystals, highlighting the applicability of the technique to nanostructured photovoltaics. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3094131]

Chalcocite (Cu$_2$S) is appealing as an absorber layer in thin film photovoltaics (PVs) due to its low cost and nearly ideal bandgap (1.2 eV). Copper is attractive compared to other common elements found in commercial PVs (i.e., silicon, cadmium, tellurium, gallium, arsenic, and indium) owing to its abundance, nontoxicity, and ease of purification. Not surprisingly, Cu$_2$S was first employed in PVs over 50 years ago.[1,2] The first thin film PVs comprised CdS/Cu$_2$S heterojunctions formed through the topotaxial exchange of Cd atoms on a CdS surface for Cu$^+$ ions in solution.[3] Interest in the technology waned in the late 1980s, however, owing to the instability of the heterojunction through which Cu$^+$ ions are prone to diffuse. In its place, the more costly ternary chalcogenide chalcopyrites (CuMX_2) (M=In, Ga and X=S, Se) have been developed, with power efficiencies now approaching 20%.[4]

Recently reports of Cu$_x$S paired with an alternative *n*-type semiconductor TiO$_2$ have shown that stable *p*/*n* heterojuctions are feasible.[5,6] As cation exchange is not possible in these Cd-free PVs, alternative deposition methods for Cu$_x$S are required. More specifically, chalcocite (Cu$_x$S, $x \sim 2$) is heavily favored for PV application among a sizeable number of copper-poor polymorphs (Cu$_x$S, $2 \geq x \geq 1.75$) as it offers the largest spectral coverage and most appropriate conductivity.[3] In addition to traditional topotaxial growth, previous routes to phase-pure chalcocite include single-source evaporation[7] and reactive sputtering.[8] More recent reports include nanoparticle syntheses[9,10] and aerosol assisted chemical vapor deposition[11] (AACVD) (a liquid precursor delivery technique akin to spray pyrolysis). Yet a true gas phase chemical vapor deposition (CVD) route to high quality chalcocite films remains elusive. More importantly, a conformal (*not* line-of-sight) growth method compatible with nanoscale structuring is needed to ameliorate the discrepancy between the minority carrier diffusion length (20–240 nm)[12] and thickness necessary (>1 μm) for ample light harvesting

in the near IR. Surmounting this incongruity by decoupling light absorption and carrier extraction into orthogonal spatial dimensions by means of high aspect ratio architectures has been advocated in several PV fields.[13–15]

In this letter we report the gas phase CVD of phase-pure Cu$_2$S by atomic layer deposition (ALD). The self-limiting surface reaction produced by alternating exposure to bis(N,N'-di-sec-butylacetamidinato)dicopper(I) {[Cu(^{s}Bu-amd)]$_2$} and hydrogen sulfide (H$_2$S) affords conformal deposition of thin films at temperatures as low as 130 °C. Characterization of film morphology, crystallinity, and optical properties shows the as-deposited material to be well suited to application in alternative approaches to PVs.

Cu$_2$S films were grown in a custom viscous flow ALD reactor similar in design to those that have been described previously.[16] Ultrahigh purity nitrogen carrier gas continuously passes through the flow tube at a mass flow rate of 300 sccm and a pressure of 1 Torr. ALD of Cu$_2$S was performed using alternating exposures to [Cu(^{s}Bu-amd)]$_2$ (Strem, 99%) and H$_2$S (Sigma-Alrich, ≥99.5%). The [Cu(^{s}Bu-amd)]$_2$ vapor was delivered by 200 sccm nitrogen flow through a bubbler held at 110 °C while the H$_2$S pressure was reduced to ~10 Torr through a regulator. (Caution: H$_2$S is a highly explosive and toxic gas.) The ALD timing sequences can be expressed as t_1-t_2-t_3-t_4, where t_1 is the exposure time for the first precursor, t_2 is the purge time following the first exposure, t_3 is the exposure time for the second precursor, and t_4 is the purge time following the exposure to the second precursor, where units are in seconds. The timing sequence was 15-15-1-10 unless otherwise stated. To enable *in situ* measurements, a quartz crystal microbalance (QCM) was installed in the ALD reactor in place of the substrates.[16] Films were deposited on 1×2 cm^2 Si(100) and 2×2 cm^2 fused silica substrates. Prior to loading, the substrates were ultrasonically cleaned in acetone and then isopropanol and blown dry using nitrogen. Prior to the Cu$_2$S ALD, the substrates were first coated with 2 nm ALD Al$_2$O$_3$.

Film morphology was assessed with a Hitachi S4700 scanning electron microscope (SEM). X-ray diffraction

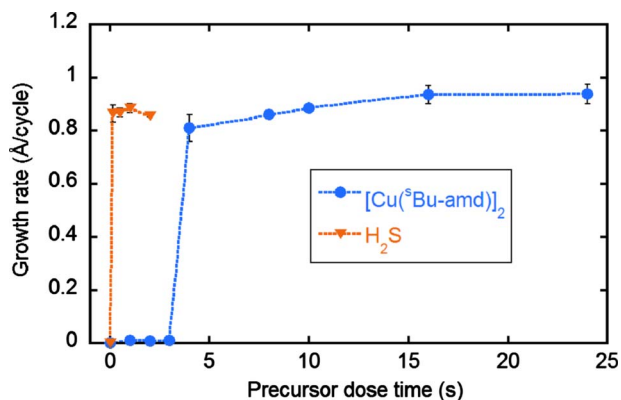a)Electronic mail: pellin@anl.gov.

FIG. 1. (Color online) Growth rate per cycle as a function of exposure time to each molecular precursor. While varying the exposure time of the alternate precursor, 10 and 1 s exposures to $[Cu(^sBu\text{-amd})]_2$ and H_2S were used, respectively.
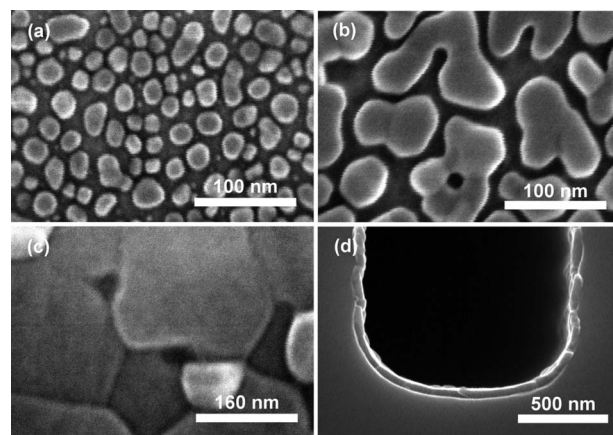

FIG. 2. SEM images of 54, 162, and 500 cycles deposited by ALD, panels [(a)–(c)], respectively. (d) Cross-sectional view of a conformal film resulting from 500 cycles on a Si trench wafer.

(XRD) measurements were acquired on a Rigaku Miniflex Plus diffractometer using Cu $K\alpha$ radiation. UV-visible-NIR reflection-corrected absorption spectra were derived from measurements employing a Varian Cary 5000 with integrating sphere accessory (DRA-2500).

The ALD of Cu_2S has recently been attempted by alternating exposure to $Cu(thd)_2$ (thd=thd~2,2,6,6-tetramethyl-3,5-heptanedione) and H_2S.[17,18] Over the range of temperatures in which the deposition was self-limiting, the growth rate does not exceed 0.4 Å/cycle and only the less desirable CuS (covellite) and/or $Cu_{1.8}S$ (digenite) phases were obtained. A pure chalcocite phase was never achieved with these precursors. In the present work, the self-limiting growth of Cu_2S employing $[Cu(^sBu\text{-amd})]_2$ is demonstrated by *in situ* QCM at 130 °C. The saturation kinetics of each half-reaction show the hallmark of authentic ALD growth (Fig. 1). A maximum growth rate of 0.94 Å/cycle was measured assuming a density of 5.8 g/cm³, corresponding to hexagonal chalcocite, (high-chalcocite, β-Cu_2S) the thermodynamically stable phase above 104 °C. The absence of decomposition (which leads to *non*-self-limiting, CVD-like growth) at this temperature is not surprising given previous reports of copper (I) nitride ALD using the same precursor at this temperature in addition to extensive characterization of the precursor family.[19,20]

The morphology of Cu_2S via ALD was revealed by SEM analysis. Images of films prepared on silicon suggest that growth occurs via island coalescence with film closure occurring between 162 and 500 ALD cycles (Fig. 2). Island growth is not unusual among ALD process and has been modeled in detail.[21] While the amount of material deposited during each cycle evolves over the first ~300 cycles with the change in surface area (a result further borne out qualitatively in QCM studies), an average growth rate of ~0.9 Å/cycle may be estimated from cross-sectional SEM analysis of a 500 cycle film, which matches well the growth rate via QCM.

The phase purity and crystallographic orientation of thin films were deduced from XRD. The pattern of the thickest (500 cycle) film may be indexed to β-Cu_2S (Ref. 22) (Fig. 3). Identical but lower intensity peaks or an absence of diffraction was observed for samples with fewer ALD cycles (not shown) suggesting instrument sensitivity limitations and/or a mostly amorphous material. Reflection indexing of

Cu_2S grown under the ALD conditions described above reveals a high preferential $\langle 00l \rangle$ orientation of the films. This preferential orientation of β-Cu_2S was also reported for films grown by AACVD. However, β-Cu_2S is known to undergo a phase change to α-Cu_2S (monoclinic, *low*-chalcocite) at temperatures below 104 °C in which the (002) β-Cu_2S crystal plane transforms to the (204) plane of the α-Cu_2S lattice.[23] While the majority of expected α-Cu_2S reflections are absent in the oriented thin films, previous studies have demonstrated reflections consistent with α-Cu_2S upon film detachment by sonication.[11] Owing to the highly adherent films produced by ALD in the present study, this elaboration was not possible.

The suitability of ALD α-Cu_2S thin films for application in PV is further established by UV-visible-NIR spectroscopy. In contrast to XRD and electrical characterization, the extent of copper deficiency in Cu_xS may be probed for very thin films, even prior to crystallite formation or island coalescence. The optical assignment of Cu_xS single crystal polymorphs ($2 \geq x \geq 1.75$) is enabled by previous detailed spectroscopic studies.[24] In the present work, the absorbance spectra of samples were found to correlate with the absorbance of these previously reported single crystal polymorphs, (Fig. 4). The similarities suggest that, like single crystals, Cu_2S grown by ALD is prone to copper depletion under ambient conditions, apparently in proportion to its surface area to volume ratio. Indirect (1.2 eV) and direct (1.3 and 1.8 eV) bandgaps for the 500 cycle sample were estimated
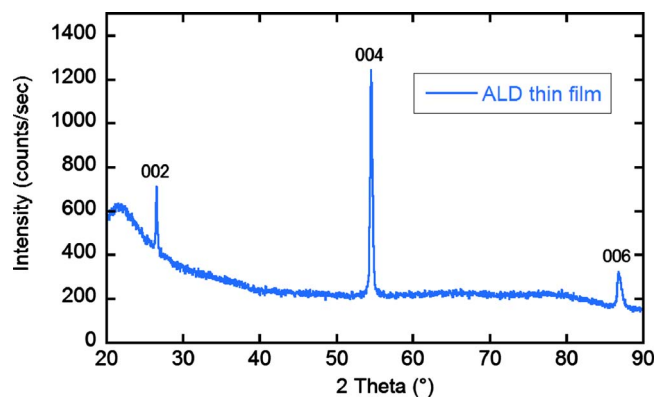

FIG. 3. (Color online) XRD pattern of 500 cycle chalcocite film on fused silica indexed to β-Cu_2S (Ref. 22).
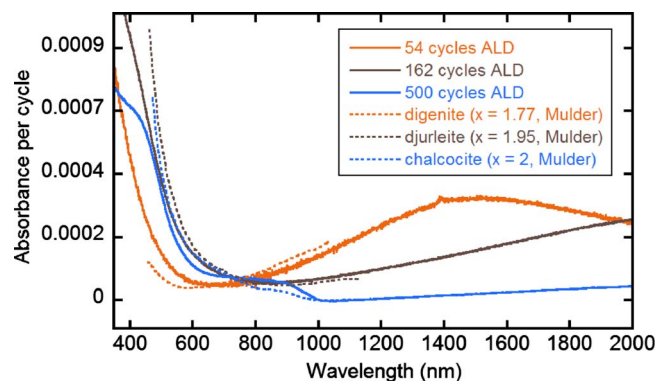
FIG. 4. (Color online) Absorbance per cycle of Cu_xS grown by 52, 162 (measured after aging in ambient overnight) and 500 ALD cycles (measured within 1 h), solid lines. The reproduction of polarization-averaged absorption coefficients (dotted lines, see Ref. 24) are shown scaled for comparison to the corresponding ALD sample.

from plots of $(\alpha h\upsilon)^{1/2}$ and $(\alpha h\upsilon)^2$ versus $h\upsilon$ plots, respectively (not shown), in agreement with literature values.[12]

The CVD of chalcocite was realized by ALD. A maximum growth rate of ~0.9 Å/cycle at 130 °C was measured from both *in situ* QCM and cross-sectional SEM analysis. XRD and optical spectroscopy confirm the phase purity of the preferentially orientation thin films. The growth of high quality and *conformal* Cu_2S films make this process a promising route to nanostructured photovoltaics.

[1] D. C. Reynolds, C. Leies, L. L. Antes, and R. E. Marburger, Phys. Rev. **96**, 533 (1954).
[2] F. A. Shirland, Advanced Energy Conversion **6**, 201 (1966).
[3] F. Pfisterer, Thin Solid Films **431**, 470 (2003).
[4] I. Repins, M. A. Contreras, B. Egaas, C. DeHart, J. Scharf, C. L. Perkins, B. To, and R. Noufi, Prog. Photovoltaics **16**, 235 (2008).
[5] L. Reijnen, B. Meester, A. Goossens, and J. Schoonman, Mater. Sci. Eng., C **19**, 311 (2002).
[6] G. M. Liu, T. Schulmeyer, A. Thissen, A. Klein, and W. Jaegermann, Appl. Phys. Lett. **82**, 2269 (2003).
[7] A. C. Rastogi, Saji Salkalachen, and V. G. Bhide, Thin Solid Films **52**, 1 (1978).
[8] E. Vanhoecke and M. Burgelman, Thin Solid Films **112**, 97 (1984).
[9] M. C. Brelle, C. L. Torres-Martinez, J. C. McNulty, R. K. Mehra, and J. Z. Zhang, Pure Appl. Chem. **72**, 101 (2000).
[10] Y. Wu, C. Wadia, W. Ma, B. Sadtler, and A. P. Alivisatos, Nano Lett. **8**, 2551 (2008).
[11] S. Schneider, J. R. Ireland, M. C. Hersam, and T. J. Marks, Chem. Mater. **19**, 2780 (2007).
[12] L. D. Partain, P. S. McLeod, J. A. Duisman, T. M. Peterson, D. E. Sawyer, and C. S. Dean, J. Appl. Phys. **54**, 6708 (1983).
[13] K. O. Sylvester-Hvid, S. Rettrup, and M. A. Ratner, J. Phys. Chem. B **108**, 4296 (2004).
[14] B. M. Kayes, H. A. Atwater, and N. S. Lewis, J. Appl. Phys. **97**, 114302 (2005).
[15] A. B. F. Martinson, J. W. Elam, J. Liu, M. J. Pellin, T. J. Marks, and J. T. Hupp, Nano Lett. **8**, 2862 (2008).
[16] J. W. Elam, M. D. Groner, and S. M. George, Rev. Sci. Instrum. **73**, 2981 (2002).
[17] L. Reijnen, B. Meester, A. Goossens, and J. Schoonman, Chem. Vap. Deposition **9**, 15 (2003).
[18] L. Reijnen, B. Meester, F. de Lange, J. Schoonman, and A. Goossens, Chem. Mater. **17**, 2724 (2005).
[19] Z. W. Li and R. G. Gordon, Chem. Vap. Deposition **12**, 435 (2006).
[20] Z. W. Li, S. T. Barry, and R. G. Gordon, Inorg. Chem. **44**, 1728 (2005).
[21] O. Nilsen, C. E. Mohn, A. Kjekshus, and H. Fjellvag, J. Appl. Phys. **102**, 024906 (2007).
[22] JCPDS Card No. 26–1116.
[23] M. Leon, N. Terao, and F. Rueda, Phys. Status Solidi A **67**, K11 (1981).
[24] B. J. Mulder, Phys. Status Solidi A **13**, 79 (1972).